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# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-273665

(43)Date of publication of application : 18.10.1996

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(51)Int.Cl. H01M 4/58

(21)Application number : 07-093201 (71)Applicant : MITSUI MINING & SMELTING CO LTD

(22)Date of filing : 28.03.1995 (72)Inventor : NUMATA KOICHI  
SAKAKI CHIE  
YAMANAKA SHOJI

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## (54) POSITIVE ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERY AND ITS MANUFACTURE AND LITHIUM SECONDARY BATTERY USING IT

### (57)Abstract:

PURPOSE: To provide a positive electrode material for a lithium secondary battery whose discharge cycle characteristic can be improved, its manufacturing method and the lithium secondary battery using it.

CONSTITUTION: Cobalt in lithium cobaltate having a layered structure is substituted with manganese and lithium according to  $3\text{Co}^{3+} \leftrightarrow 2\text{Mn}^{4+} + \text{Li}^+$ , and a chemical formula is expressed by  $\text{Li} (\text{Li}_x\text{Mn}_{2x}\text{Co}_{1-3x}) \text{O}_2$  ( $0 < x < 1/3$ ).

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### LEGAL STATUS

[Date of request for examination] 06.08.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

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JP08273665

**POSITIVE ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERY  
AND ITS MANUFACTURE AND LITHIUM SECONDARY BATTERY USING IT**  
MITSUI MINING & SMELTING CO LTD

**Inventor(s): ;NUMATA KOICHI ;SAKAKI CHIE ;YAMANAKA SHOJI**  
**Application No. 07093201 , Filed 19950328 , Published 19961018**

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**Int'l Class:** H01M00458

MicroPatent Reference Number: 001300072

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3. In the drawings, any words are not translated.

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**CLAIMS**

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[Claim(s)]

[Claim 1] Positive-electrode material for lithium secondary batteries characterized by for the cobalt of the cobalt acid lithium which has the layer structure being replaced by manganese and the lithium according to  $3\text{Co}^{3+}\leftrightarrow 2\text{Mn}^{4+} + \text{Li}^+$ , and expressing a chemical formula with  $\text{Li}(\text{Li}_x\text{Mn}_{2x}\text{Co}_{1-3x})\text{O}_2 (0 < x < 1/3)$ .

[Claim 2] The manufacture method of a positive-electrode material for lithium secondary

batteries according to claim 1 characterized by adding and calcinating still more superfluous lithium salt as brewing composition chemical formula  $\text{Li}(\text{Li}_x\text{Mn}_{2x}\text{Co}_{1-3x})\text{O}_2$ .

[Claim 3] The lithium secondary battery using a positive-electrode material for lithium secondary batteries according to claim 1.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the positive-electrode material used for a lithium secondary battery, especially a nonaqueous electrolyte rechargeable battery, its manufacture method, and the lithium secondary battery using this.

[0002]

[Description of the Prior Art] In recent years, portable-izing of electronic equipment, such as an AV equipment or a personal computer, and cordless-ization are progressing quickly, and small and the demand to the rechargeable battery which is lightweight and has high-energy density are high as these power supplies for a drive.

[0003] A non-drainage system rechargeable battery, especially a lithium secondary battery have the great expectation as a cell which especially has a high voltage and high-energy density at such a point. The research and development of the  $\text{LiMn}_2\text{O}_4$  grade of  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , or Spinel structure from which a lithium can be inserted and it can be desorbed as a positive-active-material material which fills the above-mentioned request are done briskly.

[0004] However,  $\text{LiXCoO}_2$  has the technical problem that contact of an active material and an electric conduction agent becomes inadequate, consequently capacity deteriorates in connection with a charge-and-discharge cycle by expansion of an electrode and the repeat of contraction while own reversibility of an active material falls, since change of the crystal structure in the process of the intercalation of a lithium and a day intercalation is large. Moreover, although it is not a technical non-technical problem, cobalt is expensive and the point which has misgiving in supply is also a problem.

[0005]

[Problem(s) to be Solved by the Invention] this invention cancels the technical problem of these conventional technology, and aims at offering the positive-electrode material for lithium secondary batteries which can raise a charge-and-discharge cycle property, its manufacture method, and the lithium secondary battery using this.

[0006]

[Means for Solving the Problem] In order to cancel the above-mentioned technical problem, this invention introduces tetravalent manganese ion, attains stabilization of host structure, and enables improvement in a charge-and-discharge cycle property.

[0007]  $\text{LiCoO}_2$  belonging to space group  $\text{R}3\text{m}$  wholeheartedly this invention person etc. as a result of research The substitution of  $3\text{Co(es)}3+ \rightarrow \text{Li}++2\text{Mn}^{4+}$  is possible between  $\text{Li}_2\text{MnO(s)}_3$  (if it rewrites  $\text{Li} (\text{Li}_1 / 3\text{Mn} 2/3) \text{O}_2$ ) belonging to space groups  $\text{C}2/\text{m}$ . It finds out that it is possible to form complete-solid-solution  $\text{Li}(\text{Li}_x\text{Mn}_{2x}\text{Co}_{1-3x})\text{O}_2$ , and

came to complete this invention.

[0008] That is, the cobalt of the cobalt acid lithium which has the layer structure is replaced by manganese and the lithium according to  $3\text{Co}_3 + \rightarrow 2\text{Mn}_4 + \text{Li}^+$ , and this invention is in the positive-electrode material for lithium secondary batteries characterized by expressing a chemical formula with  $\text{Li}(\text{LixMn}_{2x}\text{Co}_{1-3x})\text{O}_2$  ( $0 < x < 1/3$ ).

[0009] until now, although adding manganese to  $\text{LiCoO}_2$  and raising a cycle property, as shown below is reported, for the purpose of only replacing cobalt from manganese, the atomic arrangements in a crystal differ, the material of this invention is boiled clearly [the material of this invention ], and these differ clearly

[0010] for example, according to JP,4-267053,A, it is a cell using the material expressed with a general formula  $\text{LixMyNzO}_2$  (M was chosen from the group of Fe, CO, and nickel here -- it is a kind at least and N was chosen from the group of Ti, V, Cr, and Mn -- it is a kind at least), and it is proposed that a cycle property improves Moreover, according to JP,6-44973,A, it is proposed that a cycle property improves by the cell using the material which can be expressed with general formula  $\text{Li}_{y}(\text{CoyMax})\text{O}_2$  ( $x+y=1$ ). However, the thing about the material belonging to space group R3m differs from a chemical composition, and these differ from the material of this invention clearly.

[0011] In order to manufacture the positive-electrode material of this invention, lithium salt, such as a lithium carbonate, a lithium hydroxide, and a lithium nitrate, manganese compounds, such as manganese oxide, manganese carbonate, and oxy-manganese hydroxide, and cobalt compounds, such as cobalt oxide, cobalt carbonate, and cobalt hydroxide, can be used as a raw material. The target solid solution is obtained by mixing only a lithium compound as superfluous and calcinating these raw materials at 800-1000 degrees C in the atmosphere or oxygen atmosphere to a predetermined mixing ratio. In adding superfluous lithium salt having mixed and calcinated the raw material at a rate of the metallic element as the chemical formula of  $\text{Li}(\text{LixMn}_{2x}\text{Co}_{1-3x})\text{O}_2$ ,  $\text{Li}_2\text{MnO}_3$  grade generates and a single phase is because it is not obtained. Although this cause is not clear, since superfluous lithium salt fuses during baking, the liquid phase is presumed to be what helps diffusion of each metallic element.

[0012] although the lithium added superfluously remains in forms, such as a lithium hydroxide and a lithium oxide, after a reaction, it is also possible to use for the positive-electrode material of a cell as it is -- carrying out -- moreover, rinsing -- removing -- \*\*\*\* for positive-electrode material of a cell -- things are also possible

[0013]

[Function] General formula  $\text{Li}(\text{LixMn}_{2x}\text{Co}_{1-3x})\text{O}_2$  By replacing trivalent cobalt from tetravalent manganese, expansion of the grid at the time of the intercalation of a lithium and DIN TAKARESHON and contraction are suppressed, and the positive-electrode material for lithium secondary batteries obtained by this invention expressed with O2 shows a good cycle property.

[0014]

[Example] Hereafter, this invention is concretely explained based on an example.

[0015] In  $\text{Li}(\text{LixMn}_{2x}\text{Co}_{1-3x})\text{O}_2$ , it was referred to as  $x=1/6$  by using example 1 cobalt carbonate, manganese carbonate, and a lithium carbonate as a raw material, and further, it mixed by having made it change by the mole ratio with 0, 1/6, 2/6, 3/6, 4/6, 5/6, and 6/6, and the amount of superfluous lithiums was quenched after 24-hour baking at 900 degrees C. The X-ray \*\*\*\* pattern of a product is shown in drawing 1. Although the

amount of superfluous lithiums is accepted for the peak of LiCoO<sub>2</sub> and Li<sub>2</sub>MnO<sub>3</sub> by 0 and 1/6, or more by 2/6, a peak resolution is not accepted but a single phase and a bird clapper are known. That is, 2/6 or more superfluous lithium salt is required to Li(LixMn<sub>2</sub>xCo<sub>1-3</sub>x)O<sub>2</sub> at 900 degrees C to compound solid-solution Li(LixMn<sub>2</sub>xCo<sub>1-3</sub>x)O<sub>2</sub>.

[0016] It compounded completely like the example 1 except having made example 2 burning temperature into 1000 degrees C. The X-ray \*\*\*\* pattern of a product is shown in drawing 2. In the burning temperature of 1000 degrees C, a peak resolution was not accepted or more by 1/6, but the amount of superfluous lithiums became a single phase. Since it becomes burning temperature is high and easy atomic to spread this, the influence of a superfluous lithium is presumed to be what becomes small.

[0017] It compounded completely like the example 1 except having made the example 3 lithium compound into the lithium hydroxide. The X-ray \*\*\*\* pattern of a product is shown in drawing 3. Although the amount of superfluous lithiums was accepted for the peak of LiCoO<sub>2</sub> and Li<sub>2</sub>MnO<sub>3</sub> by 0 and 1/6 like the example 1, or more by 2/6, a peak resolution was not accepted but it became a single phase.

[0018] The amount of example 4 superfluous lithiums was made into 0.75x (1+x), nine stages of manganese:cobalt ratios were changed from 1:9 to 9:1, and it quenched after 24-hour baking at 900 degrees C. The X-ray \*\*\*\* pattern of a product is shown in drawing 4. It can be said that coexistence of LiCoO<sub>2</sub> and Li<sub>2</sub>MnO<sub>3</sub> is not accepted, but serves as a single phase by any \*\*\*\* pattern.

[0019] After rinsing the sample of the manganese:cobalt ratio 1:9 among the solid solutions obtained in the example 5 example 4 and removing superfluous lithium salt, the model cell shown in drawing 5 estimated the charge-and-discharge cycle property of a cell. the one-mol 4 boron-fluoride lithium was made into the cut voltage 3-4.3V and current density 1 mA/cm<sup>2</sup> at the electrolytic solution using \*\* dissolved at the mixed solvent of propylene carbonate and 1 and 2-dimethoxyethane An evaluation result is shown in Table 1. in addition, drawing 5 -- setting -- 1 -- a negative-electrode terminal and 2 -- an insulator and 3 -- a negative-electrode collecting electrode plate and 4 -- negative-electrode material and 5 -- separator and 6 -- a positive electrode -- a mixture and 7 show a positive-electrode terminal, respectively

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[0021]

[Table 1]

サイクル数	放電容量 (mAh/g)	
	実施例5	比較例1
1	140	152
25	135	141
50	132	138
100	130	128

[0022] Although the service capacity of the positive-electrode material by which 50 cycle does not replace is large so that clearly from the result of Table 1, henceforth [ 50 cycles ], the service capacity of the positive-electrode material of this invention is large, and it turns out that the lithium secondary battery using the positive-electrode material of this invention is excellent in a charge-and-discharge cycle property.

[0023]

[Effect of the Invention] As explained above, the lithium secondary battery using the positive-electrode material of this invention is excellent in the cycle property of charge and discharge. Moreover, it also has the advantage that the amount of the expensive cobalt used can be reduced.

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## TECHNICAL FIELD

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[Industrial Application] this invention relates to the positive-electrode material used for a lithium secondary battery, especially a nonaqueous electrolyte rechargeable battery, its manufacture method, and the lithium secondary battery using this.

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## PRIOR ART

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[Description of the Prior Art] In recent years, portable-izing of electronic equipment, such as an AV equipment or a personal computer, and cordless-ization are progressing quickly, and small and the demand to the rechargeable battery which is lightweight and has high-energy density are high as these power supplies for a drive.

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## EFFECT OF THE INVENTION

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## TECHNICAL PROBLEM

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## MEANS

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## OPERATION

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#### DESCRIPTION OF DRAWINGS

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##### [Brief Description of the Drawings]

[Drawing 1] The graph which shows the X diffraction pattern of the product in an example 1.

[Drawing 2] The graph which shows the X diffraction pattern of the product in an example 2.

[Drawing 3] The graph which shows the X diffraction pattern of the product in an example 3.

[Drawing 4] The graph which shows the X diffraction pattern of the product in an example 4.

[Drawing 5] The outline cross section of the model cell of the lithium secondary battery used in the example 5.

[Description of Notations]

1:a negative-electrode terminal and 2: -- an insulator, 3:negative-electrode collecting electrode plate, 4:negative-electrode material, 5:separator, and 6:positive electrode -- a mixture and 7:positive-electrode terminal

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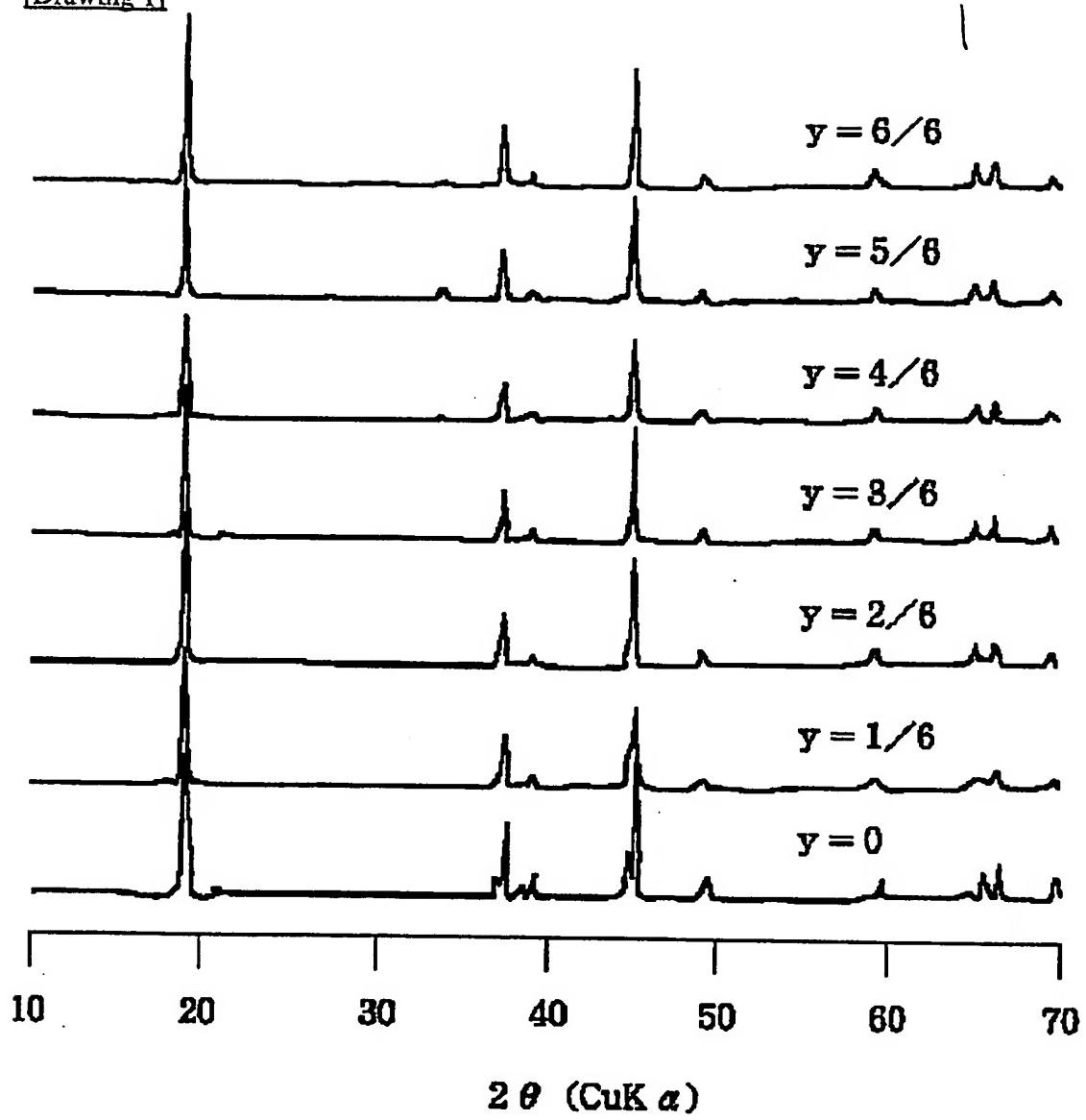
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DRAWINGS

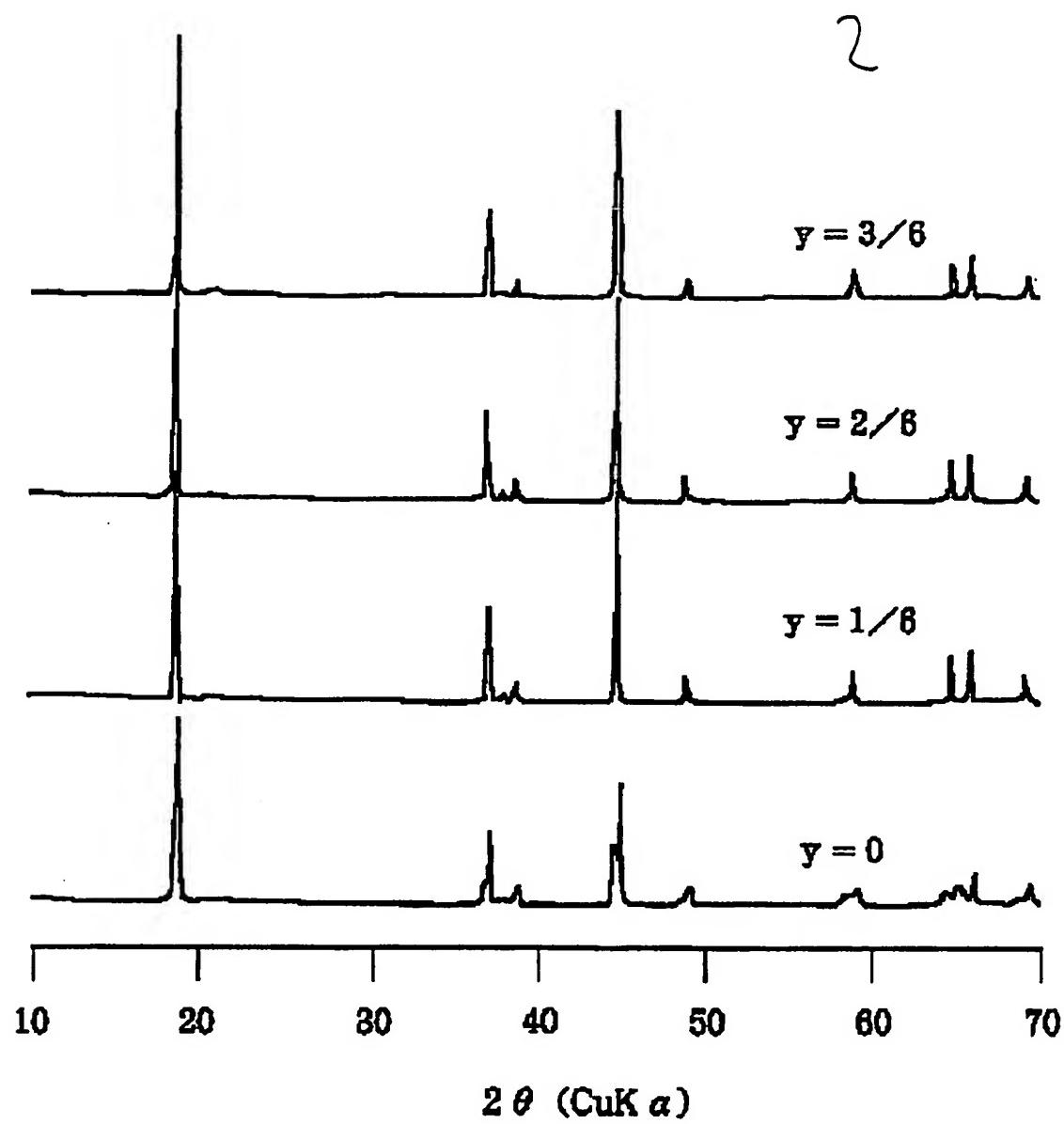
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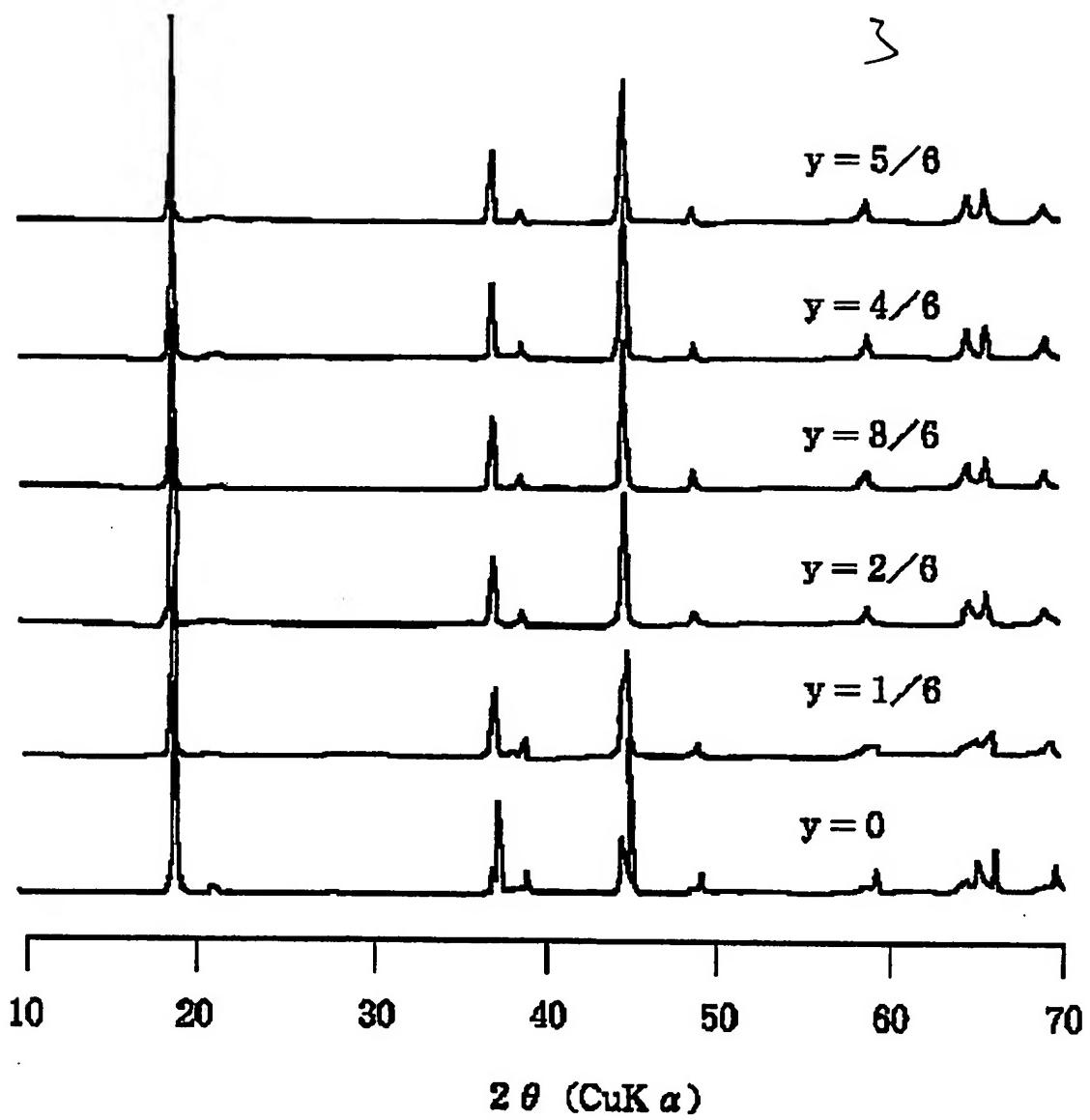
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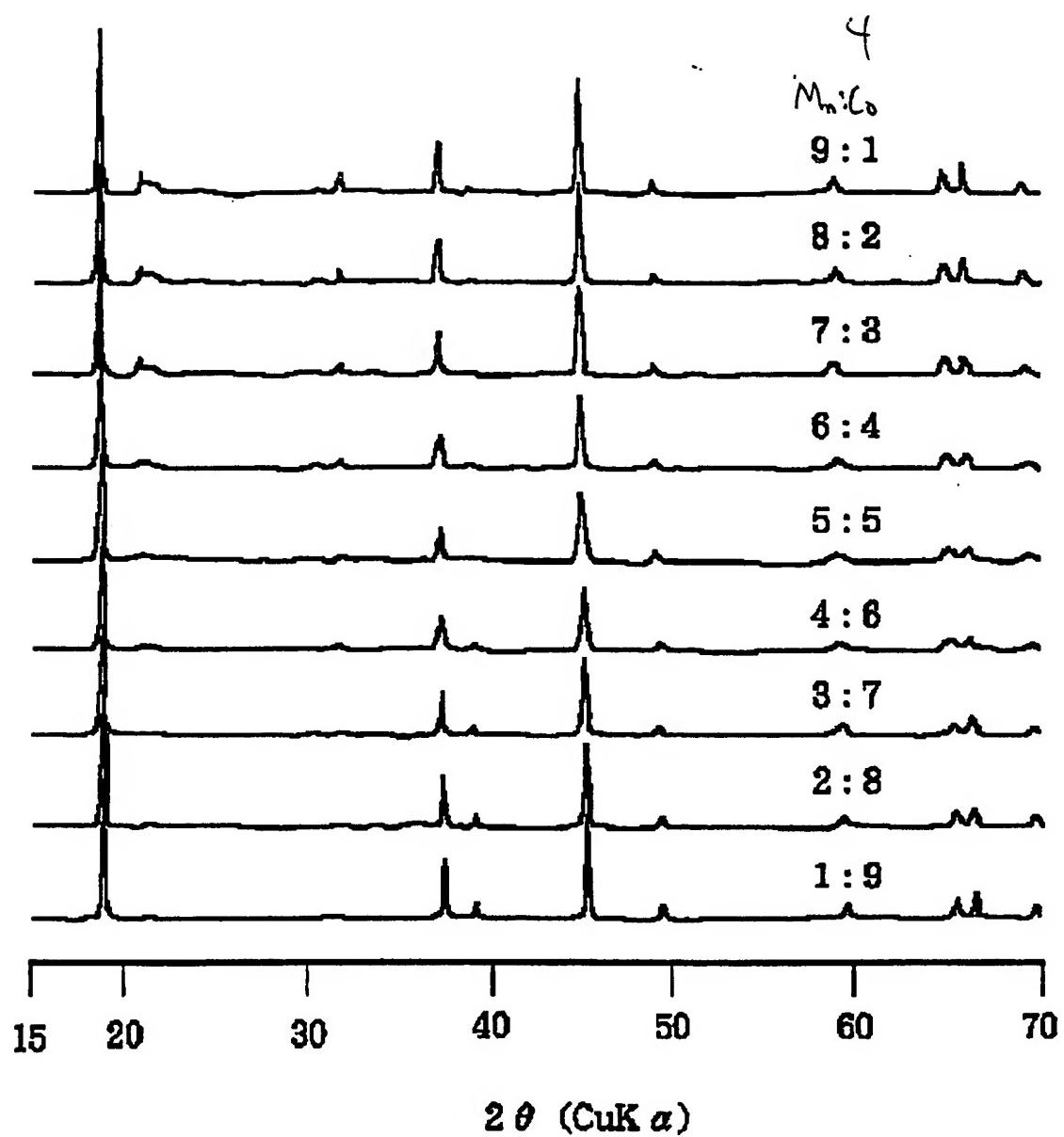
[Drawing 2]



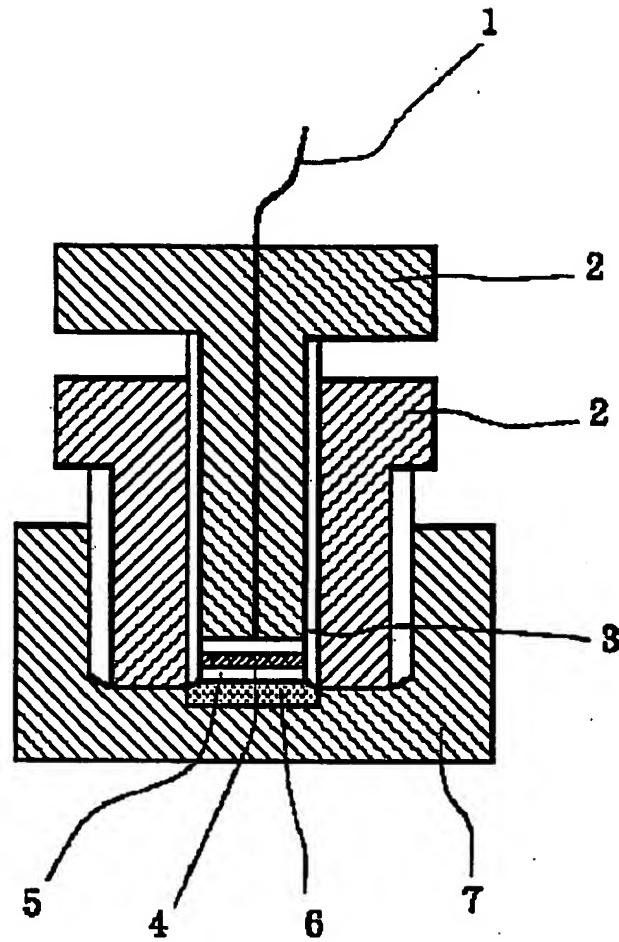
[Drawing 3]



[Drawing 4]



[Drawing 5]



(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平8-273665

(43)公開日 平成8年(1996)10月18日

(51)Int.Cl.<sup>6</sup>  
H 0 1 M 4/58

識別記号 庁内整理番号  
H 0 1 M 4/58

F I  
H 0 1 M 4/58

技術表示箇所

審査請求 未請求 請求項の数3 FD (全7頁)

(21)出願番号	特願平7-93201	(71)出願人 000006183 三井金属鉱業株式会社 東京都中央区日本橋室町2丁目1番1号
(22)出願日	平成7年(1995)3月28日	(72)発明者 沼田 幸一 広島県竹原市竹原町652-15 (72)発明者 樺 千絵 広島県東広島市西条中央3丁目26-44-306 (72)発明者 山中 昭司 広島県広島市南区南蟹屋1丁目3-35-1105 (74)代理人 弁理士 伊東 辰雄 (外1名)

(54)【発明の名称】 リチウム二次電池用正極材料およびその製造方法、並びにこれを用いたリチウム二次電池

(57)【要約】

【目的】 放電サイクル特性を向上させることができないリチウム二次電池用正極材料およびその製造方法、並びにこれを用いたリチウム二次電池を提供する。

【構成】 層状構造を有するコバルト酸リチウムのコバルトが $3\text{Co}^{3+} \longleftrightarrow 2\text{Mn}^{4+} + \text{Li}^+$ に従ってマンガンとリチウムで置換され、化学式が $\text{Li}_x\text{Mn}_{2-x}\text{Co}_{1-x}\text{O}_2$  ( $0 < x < 1/3$ ) で表されることを特徴とするリチウム二次電池用正極材料。

## 【特許請求の範囲】

【請求項1】 層状構造を有するコバルト酸リチウムのコバルトが $3\text{Co}^{3+}\longleftrightarrow 2\text{Mn}^{4+} + \text{Li}^+$ に従ってマンガンとリチウムで置換され、化学式が $\text{Li}_x(\text{Li}_{1-x}\text{Mn}_2\text{Co}_{1-x})\text{O}_2$  ( $0 < x < 1/3$ ) で表されることを特徴とするリチウム二次電池用正極材料。

【請求項2】 仕組成として化学式 $\text{Li}_x(\text{Li}_{1-x}\text{Mn}_2\text{Co}_{1-x})\text{O}_2$ に、さらに過剰のリチウム塩を添加して焼成することを特徴とする請求項1に記載のリチウム二次電池用正極材料の製造方法。

【請求項3】 請求項1に記載のリチウム二次電池用正極材料を用いたリチウム二次電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明はリチウム二次電池、特に非水電解液二次電池に用いられる正極材料とその製造方法およびこれを用いたリチウム二次電池に関する。

## 【0002】

【従来の技術】 近年、AV機器あるいはパソコン等の電子機器のポータブル化、コードレス化が急速に進んでおり、これらの駆動用電源として小型、軽量で高エネルギー密度を有する二次電池への要求が高い。

【0003】 このような点で非水系二次電池、特にリチウム二次電池は、とりわけ高電圧、高エネルギー密度を有する電池としての期待が大きい。上記の要望を満たす正極活性材としてリチウムを挿入、脱離することのできる $\text{LiCoO}_2$ 、 $\text{LiNiO}_2$ やスピネル構造の $\text{LiMn}_2\text{O}_4$ 等の研究開発が盛んに行われている。

【0004】 しかし、 $\text{Li}_1\text{CoO}_2$ は、リチウムのインターラーチング、デインターラーチングの過程での結晶構造の変化が大きいため、活性質自身の可逆性が低下すると共に、電極の膨張、収縮の繰り返しにより、活性質と導電剤の接触が不十分になり、その結果、充放電サイクルに伴い容量が劣化するという課題がある。また、技術的な未課題ではないが、コバルトは高価であり、供給に不安がある点も問題である。

## 【0005】

【発明が解決しようとする課題】 本発明は、これら従来技術の課題を解消し、充放電サイクル特性を向上させることができなりリチウム二次電池用正極材料およびその製造方法、並びにこれを用いたリチウム二次電池を提供することを目的とする。

## 【0006】

【課題を解決するための手段】 本発明は上記課題を解消するために、4価のマンガニイオンを導入しホスト構造の安定化を図り、充放電サイクル特性の向上を可能とするものである。

【0007】 本発明者等は鋭意研究の結果、空間群R 3 mに属する $\text{LiCoO}_2$ が、空間群C 2/mに属する $\text{Li}_2\text{MnO}_3$ （書き換えると $\text{Li}_1(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$

$\text{O}_2$ ）との間で $3\text{Co}^{3+}\rightarrow\text{Li}^++2\text{Mn}^{4+}$ の置換が可能であり、全率固溶体 $\text{Li}_x(\text{Li}_{1-x}\text{Mn}_2\text{Co}_{1-x})\text{O}_2$ を形成することが可能であることを見出し、本発明を完成するに至った。

【0008】 すなわち、本発明は、層状構造を有するコバルト酸リチウムのコバルトが $3\text{Co}^{3+}\longleftrightarrow 2\text{Mn}^{4+} + \text{Li}^+$ に従ってマンガンとリチウムで置換され、化学式が $\text{Li}_x(\text{Li}_{1-x}\text{Mn}_2\text{Co}_{1-x})\text{O}_2$  ( $0 < x < 1/3$ ) で表されることを特徴とするリチウム二次電池用正極材料である。

【0009】 これまでには、以下に示すように $\text{LiCoO}_2$ にマンガンを添加してサイクル特性を向上させることは報告されているが、これらは単にコバルトをマンガンで置換することを目的としたものであり、本発明の材料とは明らかに結晶内の原子配列が異なるものであり、本発明の材料とは明確に異なる。

【0010】 例えば特開平4-267053号公報によれば、一般式 $\text{Li}_x\text{M}_y\text{N}_z\text{O}_2$ （ここでMはFe、Co、Niの群から選ばれた少なくとも一種であり、NはTi、V、Cr、Mnの群から選ばれた少なくとも一種である）で表される材料を用いた電池で、サイクル特性が向上することが提案されている。また、特開平6-44973号公報によれば、一般式 $\text{Li}_x(\text{Co}_y\text{Mn}_z)\text{O}_2$  ( $x+y=1$ ) で表せる材料を用いた電池でサイクル特性が向上することが提案されている。しかし、これらは空間群R 3 mに属する材料に関するもの、あるいは化学組成が異なるものであり、本発明の材料とは明らかに異なる。

【0011】 本発明の正極材料を製造するには、炭酸リチウム、水酸化リチウム、硝酸リチウム等のリチウム塩と酸化マンガン、炭酸マンガン、オキシ水酸化マンガン等のマンガン化合物と酸化コバルト、炭酸コバルト、水酸化コバルト等のコバルト化合物を原料として用いることができる。これらの原料を所定の混合比にリチウム化合物のみ過剰として混合し、大気あるいは酸素雰囲気中で800~1000°Cで焼成することにより目的とする固溶体が得られる。過剰のリチウム塩を加えるのは、 $\text{Li}_x(\text{Li}_{1-x}\text{Mn}_2\text{Co}_{1-x})\text{O}_2$ の化学式通りの金属元素の割合で原料を混合して、焼成したのでは $\text{Li}_2\text{MnO}_3$ 等が生成して单一相は得られないためである。この原因是明らかではないが、焼成中に過剰のリチウム塩が溶融するので液相が各金属元素の拡散を手助けするものと推定される。

【0012】 反応後、過剰に加えたリチウムは水酸化リチウム、酸化リチウム等の形で残留するが、そのまま電池の正極材料に用いることも可能であるし、また水洗により除去して電池の正極材料用いることも可能である。

## 【0013】

【作用】 一般式 $\text{Li}_x(\text{Li}_{1-x}\text{Mn}_2\text{Co}_{1-x})\text{O}_2$ で表わされる本発明で得られたリチウム二次電池用正極材料は

3価のコバルトを4価のマンガンで置換することにより、リチウムのインターラーション、ディンターカレーション時の格子の膨張、収縮が抑制され良好なサイクル特性を示す。

#### 【0014】

【実施例】以下、本発明を実施例に基づいて具体的に説明する。

#### 【0015】実施例1

炭酸コバルト、炭酸マンガン、炭酸リチウムを原料として、 $L_i(L_{1-x}Mn_xCo_{1-3x})O_2$ において $x=1/6$ とし、さらに過剰リチウム量をモル比で0、 $1/6$ 、 $2/6$ 、 $3/6$ 、 $4/6$ 、 $5/6$ 、 $6/6$ と変化させて混合を行ない、 $900^\circ C$ で24時間焼成後、急冷した。図1に生成物のX線回折パターンを示す。過剰リチウム量が0、 $1/6$ では $L_iCoO_2$ 、 $L_{1/2}MnO_3$ のピークが認められるが、 $2/6$ 以上ではピーク分離が認められず、単一相となることが判る。つまり、 $900^\circ C$ で固溶体 $L_i(L_{1-x}Mn_xCo_{1-3x})O_2$ を合成するには $L_i(L_{1-x}Mn_xCo_{1-3x})O_2$ に対して $2/6$ 以上の過剰リチウム塩が必要である。

#### 【0016】実施例2

焼成温度を $1000^\circ C$ とした以外は実施例1と全く同様にして合成を行なった。図2に生成物のX線回折パターンを示す。焼成温度 $1000^\circ C$ では過剰リチウム量が $1/6$ 以上でピーク分離が認められず、単一相となつた。これは焼成温度が高く原子の拡散が容易になるため、過剰リチウムの影響は小さくなるものと推定される。

#### 【0017】実施例3

リチウム化合物を水酸化リチウムとした以外は実施例1\*

\*と全く同様にして合成を行なつた。図3に生成物のX線回折パターンを示す。実施例1と同様に過剰リチウム量が0、 $1/6$ では $L_iCoO_2$ 、 $L_{1/2}MnO_3$ のピークが認められるが、 $2/6$ 以上ではピーク分離が認められず、単一相となつた。

#### 【0018】実施例4

過剰リチウム量を $0.75 \times (1+x)$ とし、マンガン：コバルト比を1:9から9:1まで9段階変化させて $900^\circ C$ で24時間焼成後、急冷した。図4に生成物のX線回折パターンを示す。いずれの回折パターンでも $L_iCoO_2$ 、 $L_{1/2}MnO_3$ の共存は認められず、単一相となっているといえる。

#### 【0019】実施例5

実施例4で得られた固溶体のうちマンガン：コバルト比1:9の試料を水洗して、過剰のリチウム塩を除去した後、図5に示すモデルセルで電池の充放電サイクル特性を評価した。電解液には1モルの四フッ化ホウ素リチウムをプロピレンカーボネートと1,2-ジメトキシエタンの混合溶媒に溶解したものを用い、カット電圧3~4.3V、電流密度 $1mA/cm^2$ とした。表1に評価結果を示す。なお、図5において、1は負極端子、2は絶縁物、3は負極集電板、4は負極材、5はセパレータ、6は正極合剤、7は正極端子をそれぞれ示す。

#### 【0020】比較例1

マンガンを加えず、リチウム：コバルト=1:1で実施例4と同様の条件で $L_iCoO_2$ を調製し、実施例5と同様の方法で電池の充放電サイクル特性を評価した。

#### 【0021】

#### 【表1】

サイクル数	放電容量 (mAh/g)	
	実施例5	比較例1
1	140	152
25	135	141
50	132	133
100	130	128

【0022】表1の結果から明らかなように、50サイクルまでは置換を行わない正極材料の放電容量が大きいが、50サイクル以降では本発明の正極材料の放電容量が大きく、本発明の正極材料を用いたリチウム二次電池は充放電サイクル特性に優れることが判る。

#### 【0023】

【発明の効果】以上説明したように、本発明の正極材料を用いたリチウム二次電池は充放電のサイクル特性に優れる。また、高価なコバルトの使用量を低減できるという利点も有する。

#### 【図面の簡単な説明】

40 【図1】 実施例1における生成物のX線回折パターンを示すグラフ。

【図2】 実施例2における生成物のX線回折パターンを示すグラフ。

【図3】 実施例3における生成物のX線回折パターンを示すグラフ。

【図4】 実施例4における生成物のX線回折パターンを示すグラフ。

【図5】 実施例5で用いられたリチウム二次電池のモデルセルの概略断面図。

50 【符号の説明】

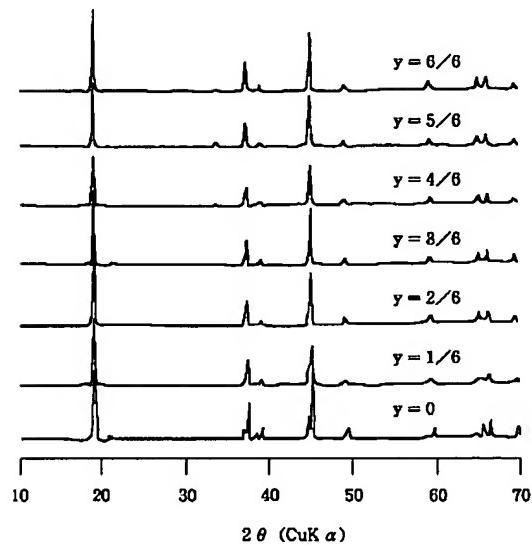
(4)

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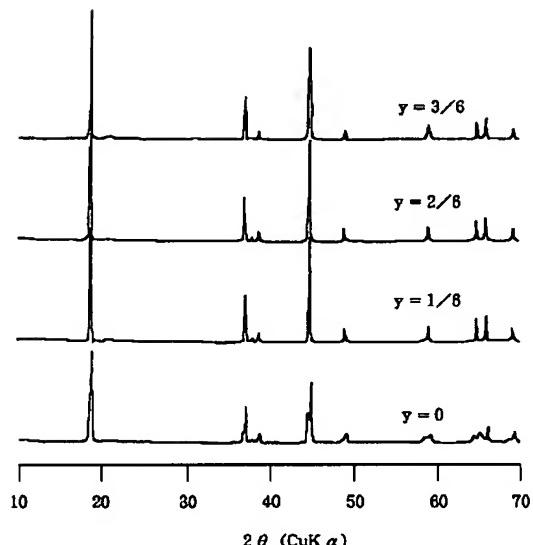
5

1 : 負極端子、2 : 絶縁物、3 : 負極集電板、4 : 負  
極材、5 : セパレータ、6 : 正極合剤、7 : 正極端子。

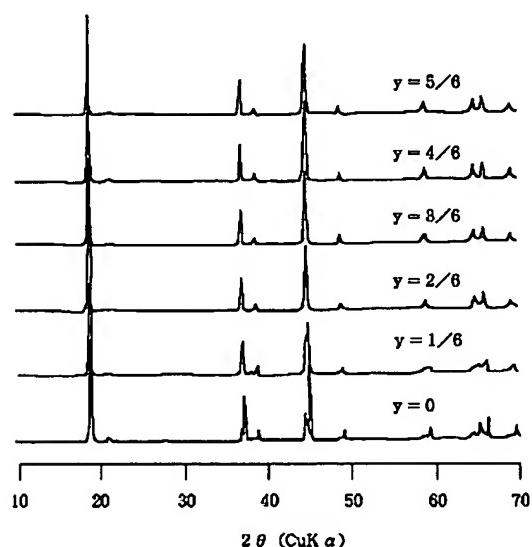
【図1】



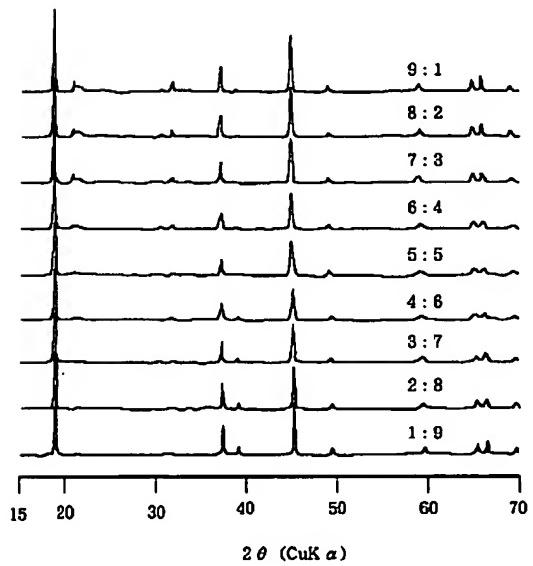
【図2】



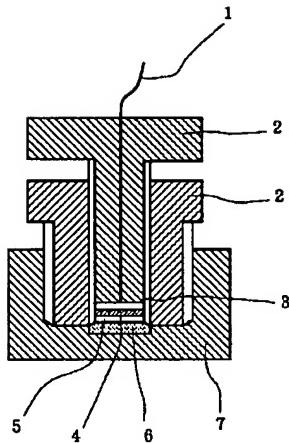
【図3】



【図4】



【図5】



## 【手続補正書】

【提出日】平成7年5月30日

## 【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】0007

【補正方法】変更

## 【補正内容】

【0007】本発明者等は鋭意研究の結果、空間群 $R\bar{3}m$ に属する $\text{LiCoO}_2$ が、空間群 $C2/m$ に属する $\text{Li}_{2-x}\text{MnO}_3$ （書き換えると $\text{Li}_{1-x}\text{Mn}_{2-x}\text{O}_3$ ）との間で $3\text{Co}^{3+} \rightarrow \text{Li}^+ + 2\text{Mn}^{4+}$ の置換が可能であり、全率固溶体 $\text{Li}_{1-x}\text{Mn}_{2-x}\text{Co}_{1-x}\text{O}_2$ を形成することが可能であることを見出し、本発明を完成するに至った。

## 【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0009

【補正方法】変更

## 【補正内容】

【0009】これまでには、以下に示すように $\text{LiCoO}_2$ にマンガンを添加してサイクル特性を向上させることは報告されているが、これらは単にコバルトをマンガンで置換することを目的としたものであり、本発明の材料とは明らかに結晶内の原子配列が異なるものであり、本発明の材料とは明確に異なる。

## 【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0019

【補正方法】変更

## 【補正内容】

## 【0019】実施例5

実施例4で得られた固溶体のうちマンガン：コバルト比

1 : 9の試料を水洗して、過剰のリチウム塩を除去した後、図5に示すモデルセルで電池の充放電サイクル特性を評価した。電解液には1モルの四フッ化ホウ素リチウムをプロピレンカーボネートと1, 2-ジメトキシエタンの混合溶媒に溶解したものを用い、カット電圧3～4.3V、電流密度 $1\text{mA}/\text{cm}^2$ とした。表1に評価結果を示す。なお、図5において、1は負極端子、2は絶縁物、3は負極集電板、4は負極材、5はセパレータ、6は正極合剤、7は正極端子をそれぞれ示す。

## 【手続補正4】

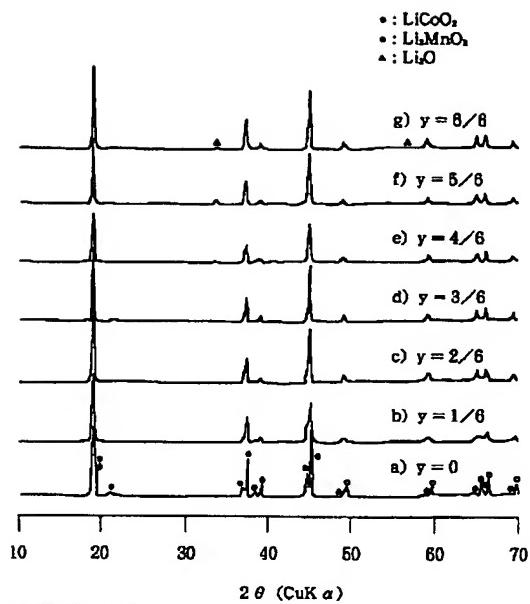
【補正対象書類名】図面

【補正対象項目名】図1

【補正方法】変更

## 【補正内容】

## 【図1】



【手続補正 5】

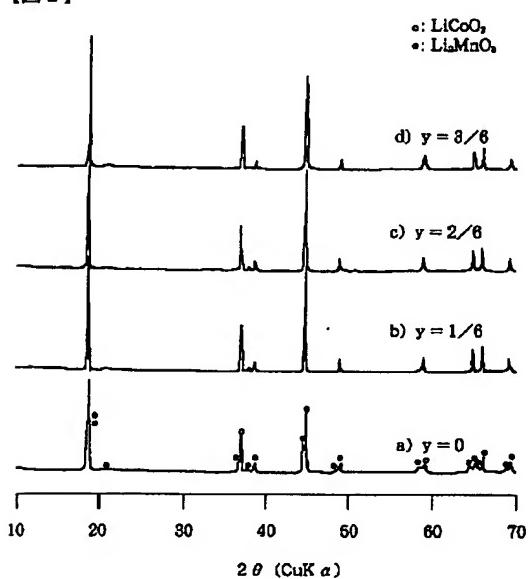
【補正対象書類名】図面

【補正対象項目名】図 2

【補正方法】変更

【補正内容】

【図 2】



【手続補正 6】

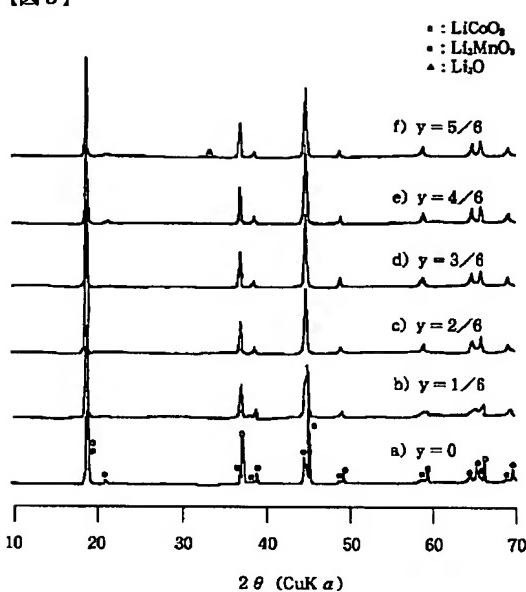
【補正対象書類名】図面

【補正対象項目名】図 3

【補正方法】変更

【補正内容】

【図 3】



【手続補正 7】

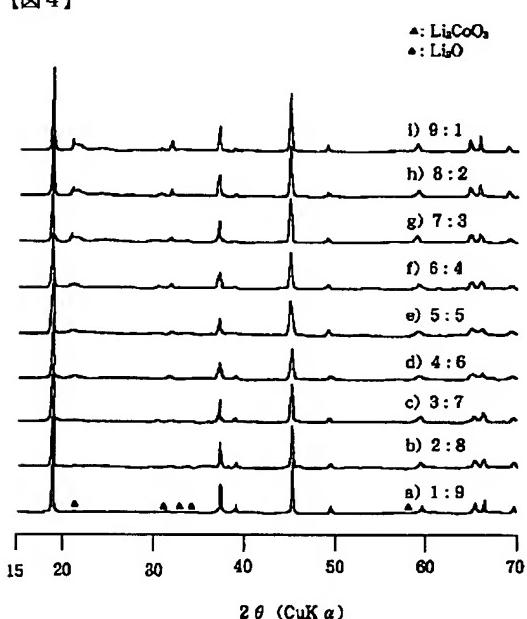
【補正対象書類名】図面

【補正対象項目名】図 4

【補正方法】変更

【補正内容】

【図 4】



## 【手続補正書】

【提出日】平成7年6月9日

## 【手続補正1】

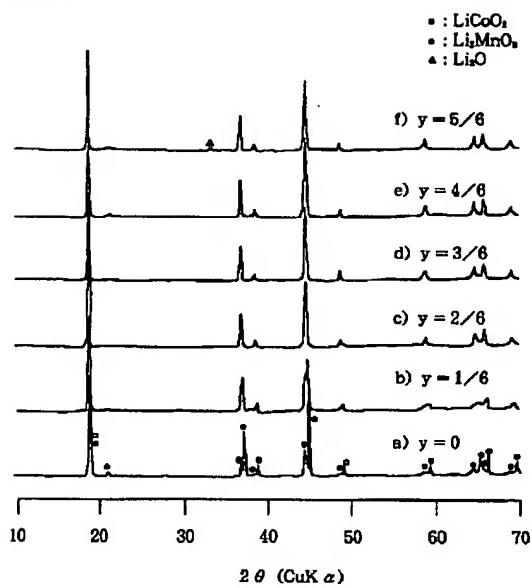
【補正対象書類名】図面

【補正対象項目名】図3

【補正方法】変更

## 【補正内容】

【図3】



## 【手続補正2】

【補正対象書類名】図面

【補正対象項目名】図4

【補正方法】変更

## 【補正内容】

【図4】

